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AUTHOR(S):

Fukuda, Kuniya; Okuda, Akizo

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# Optical Absorption Bands in $\gamma$ -Ray Irradiated LiF Crystals

Kuniya FUKUDA\*

Department of Physics, Faculty of science, Kyoto University  
and

Akizo OKUDA\*\*

Department of Mathematics and Physics, Ritsumeikan University

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The color centers produced in LiF crystals by  $\gamma$ -rays from  $\text{Co}^{60}$  have been investigated. The time rate of increase of F-centers diminished with continued  $\gamma$ -ray irradiation and that of M-centers was constant as far as the F-center concentration was lower than  $2 \times 10^{18}/\text{cm}^3$ , and further there was a square relation between the densities of both centers. The band at  $220 \text{ m}\mu$  was developed remarkably in some crystals by the exposure to F-band light and not at all in other crystals.

## INTRODUCTION

The absorption bands caused by crystal defects in various alkali halide crystals have been extensively studied<sup>1)</sup>, and the correspondence among the absorption bands in these crystals is fairly clear. In the case of LiF, such a correspondence is not so clear for some of the absorption bands owing to the following reasons: pure crystals are difficult to be obtained, various absorption bands are apt to be produced by ionizing radiation, additive coloration has not been realized in LiF crystals, and V-type bands of the crystals, which would lie on the region below  $200 \text{ m}\mu$ , are difficult to be treated with ordinary spectrophotometer. Above all, it has been considered that the appearance of the absorption band at  $220 \text{ m}\mu$  after the bleaching of F-band by F-light or thermal treatment, which was reported by Delbecq and Pringsheim, is peculiar to LiF crystals<sup>2)</sup>. We have investigated the absorption bands produced in  $\gamma$ -ray irradiated LiF crystals and examined whether these bands were characteristic or not.

In alkali halide crystals, the models of electron trapped centers have not yet been consistently established except for F-centers. As for M-center, which has been recognized as the association of one F-center and an adjacent pair of anion and cation vacancies, Overhauser and Ruechardt conceived in their Stark effect experiments that the above M-center model proposed by Seitz would be necessary to be revised<sup>3)</sup>. In spite of many experiments for M-centers, there have been few researches concerning M-center production by ionizing radiation. Then, in order to clarify the relation between F- and M-centers, we have observed the concentration of M-centers as a function of that of F-centers in  $\gamma$ -ray irradiated LiF crystals.

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\* 福田 国弥      \*\*奥田 秋三

## EXPERIMENTAL METHOD

LiF materials were purified and prepared in our laboratory from LiCl and  $\text{NH}_4\text{HF}_2$ , and single crystals were produced by Kyropoulos' method in flowing dry nitrogen gas of about 50 mm Hg pressure<sup>4)</sup>. The crystals used in the present work were classified into three species named crystals I, II and III according to preparation process and crystal growth condition. The intensity of the ultraviolet absorption, which was designated as "A absorption" by the authors<sup>4)</sup>, was weaker in crystal I than in the other two, in which the intensities of this absorption were comparable.

The samples with thickness of approximately 0.3~3 mm were cleaved from the crystals and coloration was produced at room temperature by  $\gamma$ -ray from  $\text{Co}^{60}$  giving  $2 \times 10^6$  roentgens per hour at the Institute for Chemical Research of our University. The optical absorption was measured at room temperature by Beckman DU spectrophotometer.

## RESULTS AND DISCUSSIONS

## (a) F- and M-Band

In the early stage of the coloration (at about one hour  $\gamma$ -ray irradiation), F-band at  $250\text{ m}\mu$ , a broad and weak band with a maximum at  $350\text{ m}\mu$  and much weaker M-band at  $450\text{ m}\mu$  were produced. The latter two bands gave a light yellow color to irradiated crystals. A prolonged  $\gamma$ -ray irradiation (for example, about 8 days) produced intense M-band and two weak bands with

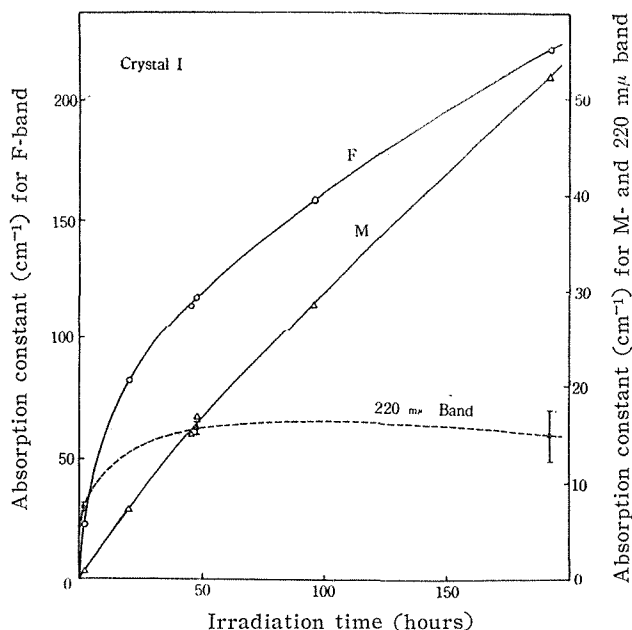


Fig. 1. Absorption constants of F-, M- and  $220\text{ m}\mu$  bands as function of  $\gamma$ -ray irradiation time.

### Absorption Bands in $\gamma$ -Ray Irradiated LiF Crystals

peaks at about  $320\text{ m}\mu$  and  $380\text{ m}\mu$  in addition to the enhanced F-band. These two bands were tentatively classified as  $R_1$ - and  $R_2$ -band respectively by Penne-  
man and powers<sup>5)</sup>. In this stage of the coloration, the crystal showed brown  
or dark brown color mainly due to M-band. Immediately after a brief ir-  
radiation, F'-band with a peak at  $620\text{ m}\mu$  was observed, but this band was  
unstable at room temperature and the prolonged irradiation did not increase  
further this band intensity.

Fig. 1 shows the absorption constants of F- and M-band as a function of  
irradiation time; F-band increases very rapidly in early stage of irradiation,  
and after about 20 hours, the rate of increase of this band decreases. In the  
X-rayed alkali halide crystals F-band is easily saturated, but in the case of LiF  
crystals F-band is not saturated even at the concentration of  $2 \times 10^{18}/\text{cm}^3$ , which  
is estimated from the Smakula's formula by assuming the oscillator strength  
of this band to be unity. As for M-band, its intensity is in general propor-  
tional to irradiation time. The relation between the concentrations of F- and  
M-centers is shown in Fig. 2, and from this figure, as far as the F-center con-  
centration is lower than  $2 \times 10^{18}/\text{cm}^3$ , the relation can be expressed approxima-  
tely as the following empirical formula :

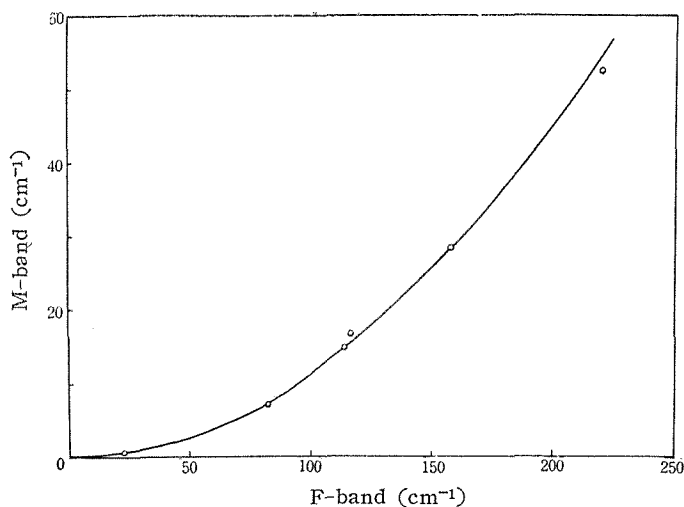


Fig. 2. The relation of absorption constants between F- and M-bands  
in  $\gamma$ -ray irradiated LiF crystals.

$$[F]^2 = k[M],$$

where  $k$  is a constant and the brackets represent the concentration of F- and  
M-centers. And if the brackets are expressed in absorption constant ( $\text{cm}^{-1}$ ),  $k$   
is about 890, but, of course, it would take a different value according to irra-  
diation conditions, for instance, the temperature of the crystals under irradia-  
tion.

#### (b) $220\text{ m}\mu$ Band

When the crystal I irradiated by  $\gamma$ -ray was exposed to the light from a low

pressure mercury lamp through KI crystal filter of about 1 mm in thickness (the light of wavelength  $254\text{ m}\mu$  was intense and the light of shorter wavelength than  $250\text{ m}\mu$  was almost absorbed by the filter), the F-band intensity was gradually reduced and the F-band peak shifted to the shorter wavelength side and finally settled down at  $220\text{ m}\mu$ . Fig. 3 shows the bleaching effect of the  $\gamma$ -rayed LiF crystal I.

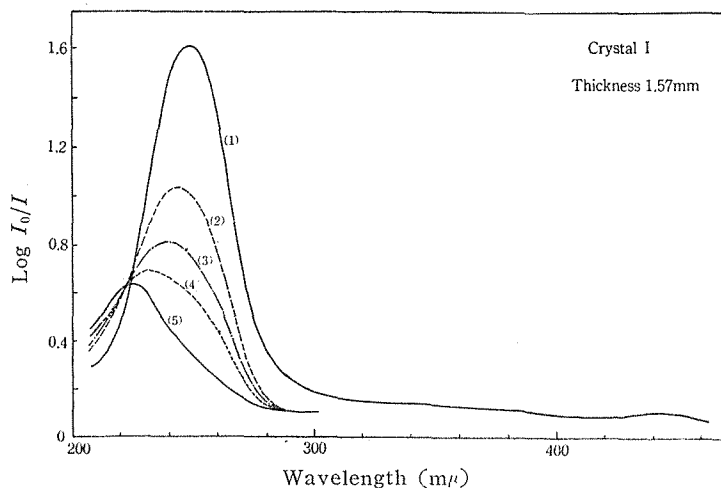


Fig. 3. F-band bleaching in LiF crystal I.

(1) 100 minutes  $\gamma$ -rays at room temperature. (2) 13 hours, (3) 7 hours, (4) 7 hours, and (5) 21 hours successive F-light irradiation at room temperature.

This band at  $220\text{ m}\mu$  is the same as that reported by Delbecq and Pringsheim<sup>2)</sup>, but when the crystal had higher concentration of F-centers by a prolonged exposure to  $\gamma$ -rays, the height of  $220\text{ m}\mu$  band relative to that of origin-

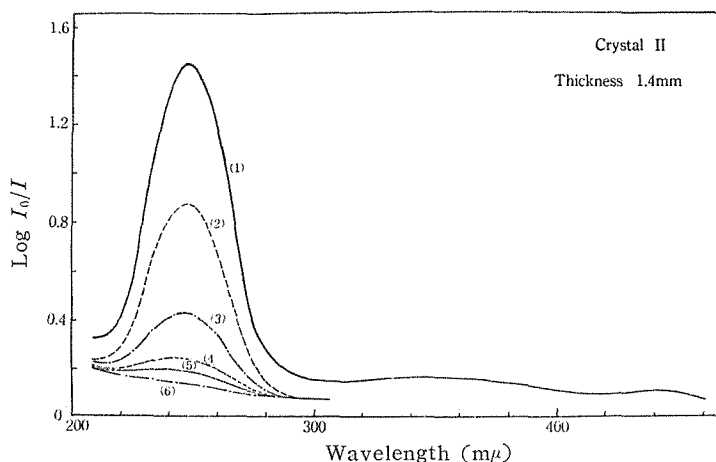


Fig. 4. F-band bleaching in LiF crystal II.

(1) 100 minutes  $\gamma$ -rays at room temperature. (2) 9.5 hours, (3) 20 hours, (4) 14 hours, (5) 7 hours, and (6) 28 hours successive F-light irradiation at room temperature.

al F-band was lowered, as Morehead and Daniels noticed in the case of LiF crystal irradiated by alpha-particles<sup>6)</sup>. The relation between the intensities of original F-band and that of 220 m $\mu$  band is shown in Fig. 1.

Contrary to the case of the crystals I, this 220 m $\mu$  band did not remain at all in the crystals II, as shown in Fig. 4, and was barely detectable in the crystals III, for the same bleaching procedures and nearly the same concentrations of F-centers as those of the crystals I.

Before the exposure to  $\gamma$ -rays, the intensity of A absorption of the crystal I is lower than those of the others, as mentioned above but the relation between the existence of A absorption and the appearance of 220 m $\mu$  band after  $\gamma$ -ray irradiation is not yet clear. Nevertheless, the result that there is the tendency of saturation in formation and the diversity of intensity in each crystal for 220 m $\mu$  band might suggest the following fact; the electrons released from F-centers are captured by some impurity atoms, or anion vacancies decomposed from F-centers are combined adjacent to the foreign atom sites, and then 220 m $\mu$  band is induced. If 220 m $\mu$  band is not intrinsic in LiF crystals, the singularity of color centers in this crystal will be reduced.

### (c) 350 m $\mu$ Band

In the early stage of  $\gamma$ -ray irradiation, the broad band with a peak at 350 m $\mu$  was produced, and after attaining to some intensity, the band was no more developed by the prolonged  $\gamma$ -ray irradiation. This band was relatively unstable at room temperature and easily destroyed by the light from a mercury lamp. This band is so broad, as shown in Fig. 5, but this seems to be a single band since it is uniformly weakened by the monochromatic light of wavelength 365 m $\mu$ . It is considered that this band might also be an absorption induced by

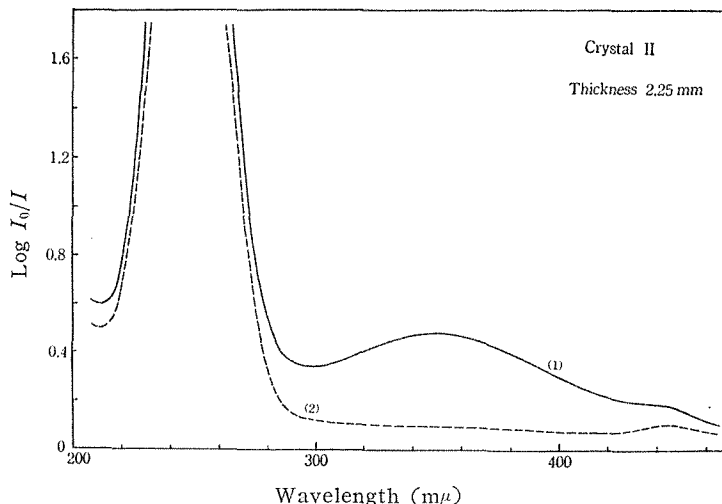


Fig. 5. 350 m $\mu$  band in  $\gamma$ -ray irradiated LiF crystal.

(1) 75 minutes  $\gamma$ -rays at room temperature. (2) 2 hours bleached by the light of the mercury lamp at room temperature.

some impurity centers contained in the crystals, but further detailed experiments will be necessary for conclusive decision.

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